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Phase Behavior of Laundry Surfactants in Polar Solvents

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ABSTRACT: Laundry surfactants are usually mixtures of ionic and nonionic detergents that exhibit a complex phase behavior. Here the ternary phase behavior of an isotropic and a liquid crystalline (LC) surfactant mixture has been examined in water/solvent systems. The size of the LC area in the ternary phase diagram was correlated to solvent parameters including the dielectric constant and the Gordon cohesiveness parameter. The Gordon parameter was found to have a linear relationship with the amount of solvent needed to go from an LC to an isotropic state over a wide range of solvents from polar to apolar. For solvents in which no surfactant aggregation (micellar or inverted micellar) is expected, the size of the LC area is linear with the reciprocal of the dielectric constant of the solvent. On diluting practical detergent liquids with water, a large LC area can be avoided by using solvents with a relatively low dielectric constant and with a relatively low molecular weight.

The aggregated state of the surfactant mixtures in the isotropic regions of the phase diagram was studied using the solvatochromic fluorescent probe Nile Red. In the water corner of the phase diagram, the surfactants are aggregated into micelles. In strongly polar solvents, such as glycerol, ethylene glycol, formamide, and ethanolamine, the surfactants are also aggregated into micelles. In somewhat less polar solvents, such as methanol, ethanol, and *t*-butanol, the surfactant molecules are randomly distributed. In the surfactant-rich corner of the phase diagram of the isotropic mixture, the surfactant forms inverted micelles. An inverted micelle-to-micelle transition could be observed on dilution in ethylene glycol as a discontinuity in the trend of the Nile Red fluorescence maxima.

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KEY WORDS: Aggregation, Nile Red, nonaqueous solvents, phase behavior, surfactant mixtures.

Laundry detergents are usually mixtures of different types of surfactants, with each surfactant component possessing

complex phase behavior. For most pure systems, the phase behavior has been studied previously (1,2), but there is a growing demand for corresponding information on mixed systems and on the phase behavior in various nonaqueous polar solvents.

In this study, the phase behavior of two surfactant mixtures was examined. Each mixture was composed of one nonionic and two ionic surfactants, a sulfonate, and a soap, making them relevant for commercial laundry applications. One of the mixtures was an isotropic liquid, whereas the other was liquid crystalline (LC). This study was focused on the aggregated state of the surfactant mixtures in the isotropic regions of the surfactant mixture/water/solvent ternary phase diagrams and on the effect of the solvent on the LC area.

LC phases are formed from pure surfactants on hydration of the head groups. Different types of mesophases have been described previously, of which the lamellar and hexagonal are the most abundant in surfactant systems (3). Besides water, some organic solvents with a high cohesive energy density (as expressed in the Hildebrand parameter) can form LC phases with surfactants (4,5). LC areas are in general smaller and simpler in polar solvents (6). For laundry purposes the formation of LC phases on dilution with water should be avoided because they often (depending on their mesophase structure) dissolve poorly in water. Therefore, information on the phase behavior in polar solvents and on the relation between solvent parameters and size of the LC area is of great importance for these applications. The type of mesophase from which the surfactant mixture becomes isotropic in various solvents was not determined, but a more empirical approach was followed.

In the isotropic regions (in which the surfactant mixture is optically clear) of a surfactant phase diagram, the surfactant molecules can be aggregated into either spherical micelles, wormlike micelles, or (small) vesicles. These systems have been called organized solutions (7). They contrast with solutions in which surfactant molecules are randomly distributed, also called random solutions (7). In water, most single-tailed surfactant molecules are organized into micelles with hydrophobic interactions as the driving force for

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Abbreviations: CMC, critical micelle concentration; LAS, linear alkylbenzene sulfonic acid; LC, liquid crystalline; MEA, monoethanolamine; λ_{max} , Nile Red maximum emission wave length.

aggregation. Aggregates in nonaqueous solvents (polar and apolar) are usually much smaller than those in water and possess small aggregation numbers (4). In apolar solvents, surfactants can be organized into inverted micelles, with dipole-dipole interactions of the head groups as the driving force. Furthermore, in apolar solvents, hanklike (small cylindrical) inverted micelles are formed rather than spherical inverted micelles (8).

The morphology of the aggregated surfactants in the isotropic regions of the phase diagram was studied using fluorescence spectroscopy. The solvatochromic fluorescent probe Nile Red (9) was found to be highly efficient for its capability to identify different aggregate morphologies in the optically isotropic region of the phase diagram (10). Nile Red has been used previously in ternary surfactant systems (11,12). The probe molecule is soluble in a wide range of solvents and shows a large bathochromic absorbance shift with increasing solvent polarity (13). Interestingly, the large solvatochromic shift makes it possible to selectively excite probe molecules in different environments. In inverted micelles, Nile Red is situated in the interface, facing the water pool, and can be selectively excited without exciting Nile Red molecules that are located either in the tail region of the surfactants or free in the apolar solvent (14). Similarly, Nile Red molecules that are located more toward the tail region of the surfactant molecules, either in micelles or in inverted micelles, can be selectively excited without exciting Nile Red in a more polar environment. These properties of the probe lead to an excitation-dependent emission maximum (λ_{max}) when different microdomains (e.g., micelles or inverted micelles) are present. If there is no aggregation of the surfactant molecules, as, for example, below the critical micelle concentration (CMC) or in a solvent in which surfactant molecules are randomly mixed (7), no excitation-dependent emission is found.

Combining the phase behavior and the morphological characteristics provides an impression of the phase changes that occur on diluting highly concentrated surfactant/solvent solutions for laundry purposes.

EXPERIMENTAL PROCEDURES

Nile Red was obtained from Acros (Landsmeer, The Netherlands). A 2.5-mM Nile Red stock solution was made in ethanol and diluted 1000-fold in the surfactant systems. Nonionic detergent Neodol 1-5 (C_xEO_y , with x on average 11, y on average 5) was obtained from Shell Chemicals; linear alkylbenzene sulfonic acid (LAS) was obtained from Lever Brothers Ltd. (Port Sunlight, United Kingdom); isostearic acid, Prisorine 3509, was obtained from Unichema (Gouda, The Netherlands); and linear fatty acid (on average C_{18}), Prifac 5908, was obtained from Unichema. Monoethanolamine (MEA) was obtained from BASF. All surfactants used were of technical grade; all other chemicals were of analytical grade.

Surfactant mixture A consisted of a mixture of nonionic

Neodol 1-5, LAS, and isostearic acid (mol ratio 37:38:25) neutralized with 10 mol% excess of MEA. Surfactant mixture B consisted of nonionic Neodol 1-5, LAS, and linear fatty acid (mol ratio 34:35:31) neutralized with 10 mol% excess of MEA.

Phase diagrams were made by dilution along the solvent axis and along 20%-water and 10%-solvent lines (w/w). The borders between the optically isotropic phases and the first signs of the LC phases were noted.

Nile Red fluorescence was measured on a SPF-500c spectrofluorometer (SLM Aminco) at 25°C, using an excitation wavelength between 490 and 590 nm. Fluorescent emission was measured from 550 to 700 nm with a 5-nm interval. The Nile Red emission maximum (λ_{max}) was calculated using a log normal fit. A 5-nm step size for the emission was found to be sufficient to obtain a resolution of several tenths of a nanometer after a log normal fit.

RESULTS

Ternary phase diagrams. The ternary phase behaviors of mixture A and mixture B were determined visually by mixing the surfactant with solvent/water mixtures until an isotropic liquid was obtained. Mixture A, which is an isotropic liquid, became LC on the addition of 5.7% (w/w) water (Fig. 1a). Up to 80% water, mixture A is LC. The types of mesophases formed were not determined, but certainly different states were present. The effect of mixing different solvents (water/solvent mixtures) is large. In mixture A, some polar solvents (glycerol, formamide, and MEA) give an LC phase even without water, resulting in a relatively large LC area. It is known that glycerol and formamide cause surfactants to aggregate into micelles at low surfactant concentrations (15). In less polar solvents, such as methanol, ethanol, propylene glycol, and *t*-butanol, the surfactants remained isotropic on dilution along the solvent axis and the size of the LC area is rather small. Ethylene glycol, in which surfactant aggregation has been observed (15), has a relatively large LC area, but surfactant mixture A remained isotropic on dilution with this solvent.

The ternary phase behavior of surfactant mixture B is significantly different from that of mixture A because it is LC prior to dilution with any solvent, due to the carboxylic acid with a linear tail instead of a branched one. Upon the addition of water, mixture B becomes isotropic at 57.4% (w/w) of water. The disappearance of the LC phase on the solvent axis was examined for a large panel of solvents, from those that are very polar such as water and formamide (Fig. 1b) to those that are very apolar such as *n*-hexane. For each solvent the mol% solvent on the border between LC and isotropic was calculated (Fig. 1c) and plotted against the reciprocal of the solvent dielectric constant ($1/\epsilon$ is linear with charge-charge interactions) and the Gordon parameter (cohesiveness parameter, with units of surface tension/molar volume^{1/3}) (16) (Fig. 2). A linear relationship was found between the size of the LC area and the recip-

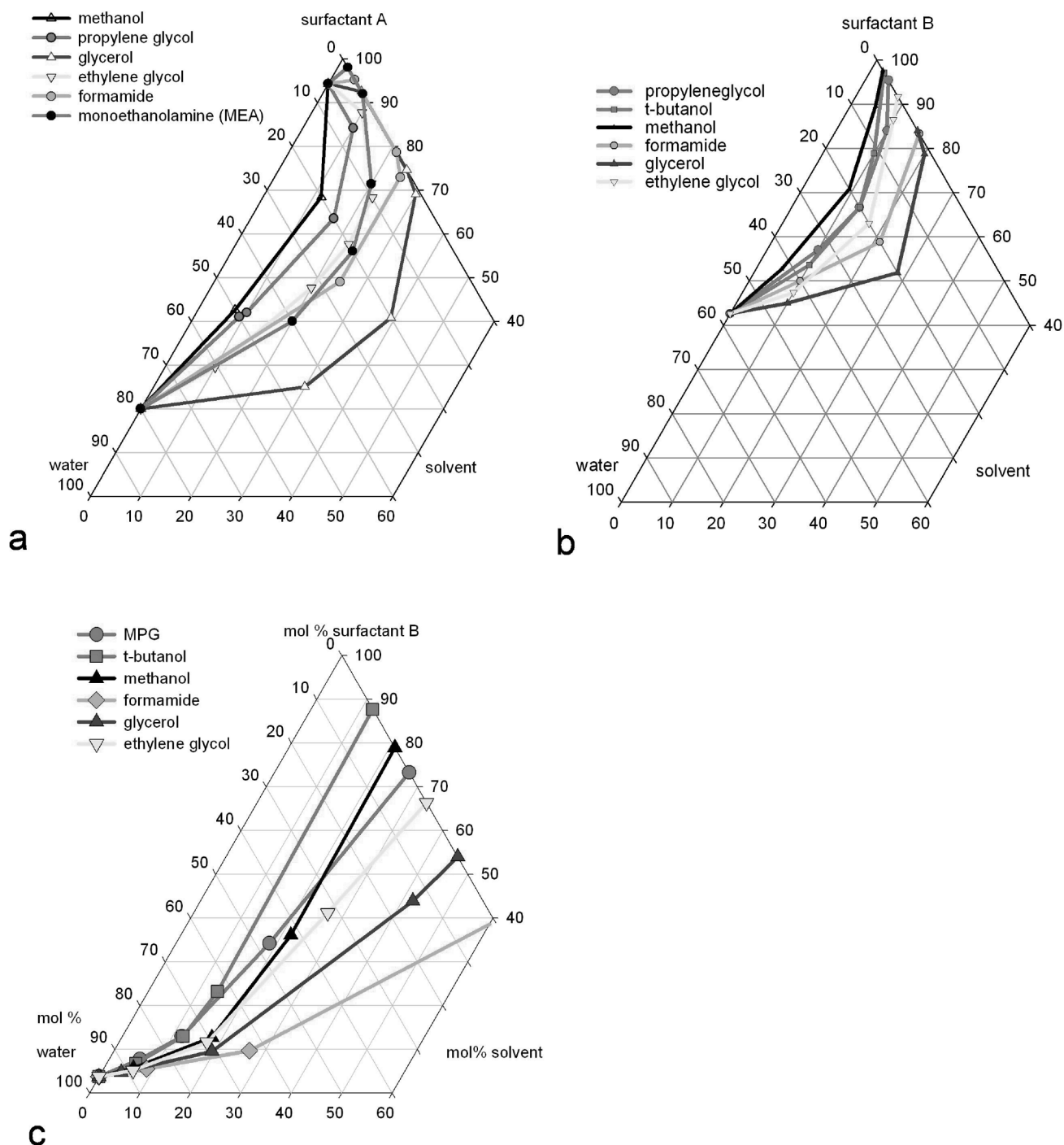


FIG.1. Ternary phase behavior of surfactant mix A and B in various solvents/water systems (weight fractions a,b, mole fractions c). Mix A is isotropic in the surfactant-rich top, a, whereas Mix B is liquid crystalline, b,c.

cal of the dielectric constant for polar solvents in which no surfactant aggregation takes place (methanol to *t*-butanol). This was further investigated by examining the effect on the LC area of different mixtures of methanol and *t*-butanol (inset Fig. 2a). Again a linear relationship was found. A large increase in the size of the LC region was found for solvents in which surfactant aggregation takes place already in the pure solvent, both on the polar side (normal micelles) and on the apolar side (inverted micelles). For all

solvents the Gordon parameter shows a good linear correlation with the size of the LC area ($R^2 = 0.98$) (Fig. 2b) on dilution of surfactant mixture B with pure solvents. Only *n*-hexane deviates from the plot, and this is the only solvent used in which inverted micelles are formed.

Both the dielectric constant and the Gordon parameter of a solvent or solvent mixture can thus be used to predict the size of the LC area. For mixtures with water, the influence of water is much stronger than expected. For any point

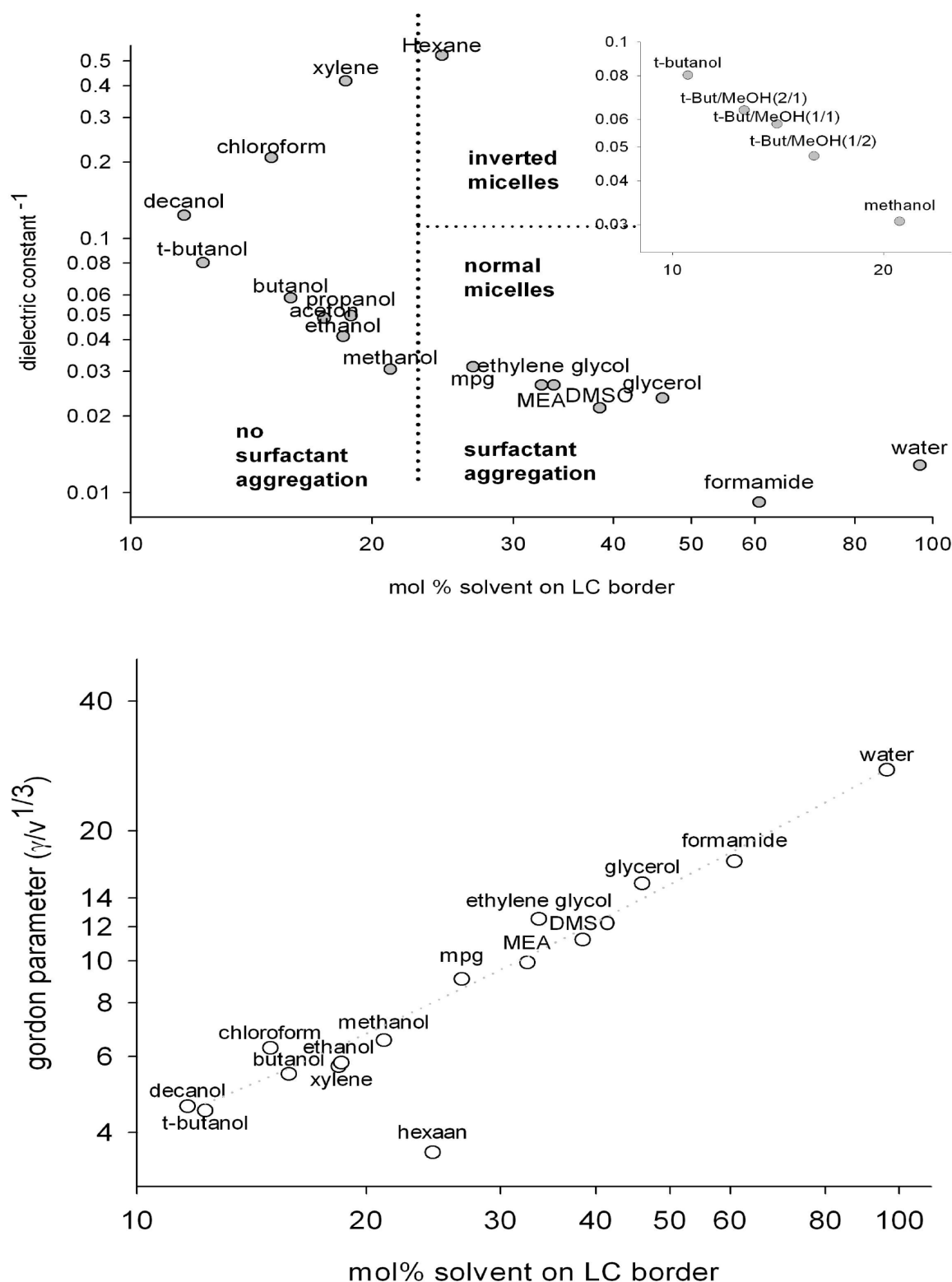


FIG. 2. mol% solvent on the border between liquid-crystalline and optically isotropic phase of surfactant mix B for both dielectric constant and Gordon parameter of the used solvents. On basis of the Nile Red measurements about the aggregated state in different solvents the graph could be divided into three regions, surfactant aggregation into normal micelles, solvents in which no surfactants aggregation takes place and the formation of inverted micelles.

in the ternary phase diagram, the LC area is larger than anticipated on the basis of ideal mixing and estimates of the surface tension and molar volume.

Nile Red. We used the fluorescent solvatochromic probe

Nile Red to establish the surfactant aggregated state. Nile Red is very useful for this purpose because it can give information for every optical isotropic region in the ternary phase diagram even in 100% surfactant mixture A. Excita-

tion-dependent fluorescence was used to determine different aggregation states within the suspensions. In aqueous solution, micelles are obviously formed. Because Nile Red is only slightly soluble in water, it will be localized either on the micellar interface or more toward the micellar core. By selective excitation of the Nile Red molecules bound more toward the micellar core, the Nile Red maximum emission wavelength (λ_{\max}) will be lower, reflecting a more apolar region. By contrast, Nile Red molecules that are excited at binding sites more toward the interface, facing water, show a larger λ_{\max} . Accordingly, when the surfactant mixture is dissolved in *n*-hexane, inverted micelles will be formed. Again Nile Red can be located in the head group region facing water or more deeply in the tail region. Because Nile Red has a high solubility in *n*-hexane, a much more excitation-dependent emission was found in that solvent (Fig. 3). In solvents in which no surfactant aggregation is expected to occur and the surfactant molecules are randomly distributed (7), the values for λ_{\max} were expected to be independent of the excitation wavelength. This is indeed the case in methanol (Gordon parameter 6.55 mN/m²) (Fig. 4) and in many other solvents with a Gordon parameter lower than approximately 9 mN/m². Propylene glycol is somewhat intermediate (Gordon parameter 9.1 mN/m²) between the

solvents in which surfactant aggregation is confirmed [Gordon parameter above 12.5 mN/m², according to Evans and Miller (15)] and solvents in which no aggregation takes place. The phase of the surfactant mixture in a solvent, micelle or inverted micelle, can be deduced from Figure 2.

To determine the aggregation state of pure surfactant mixture A, a series of dilutions were made in different solvents. Changes in the aggregation state should be reflected by a change in micropolarity, and in the λ_{\max} of Nile Red. This has been tested for pure nonionic detergents for which the phase diagram is known (1), and indeed a discontinuity was found when C₁₂EO₄ in the L2 state (inverted micelles) was diluted with water/solvent to form the L1 state (normal micelles) (10).

Upon dilution of surfactant mixture A in *n*-hexane, the λ_{\max} of Nile Red does not change from 100 mol% surfactant down to 4 mol% surfactant. Further dilution of surfactant results in a strong decrease of the λ_{\max} value, until it reaches the minimum observed value of λ_{\max} of 525 nm in *n*-hexane. Because one of the reference points is that inverted micelles are formed in a strongly apolar medium, such as *n*-hexane, it is likely that the isotropic surfactant mixture itself is organized in inverted micelles. When the surfactant mixture was diluted with ethylene glycol, λ_{\max}

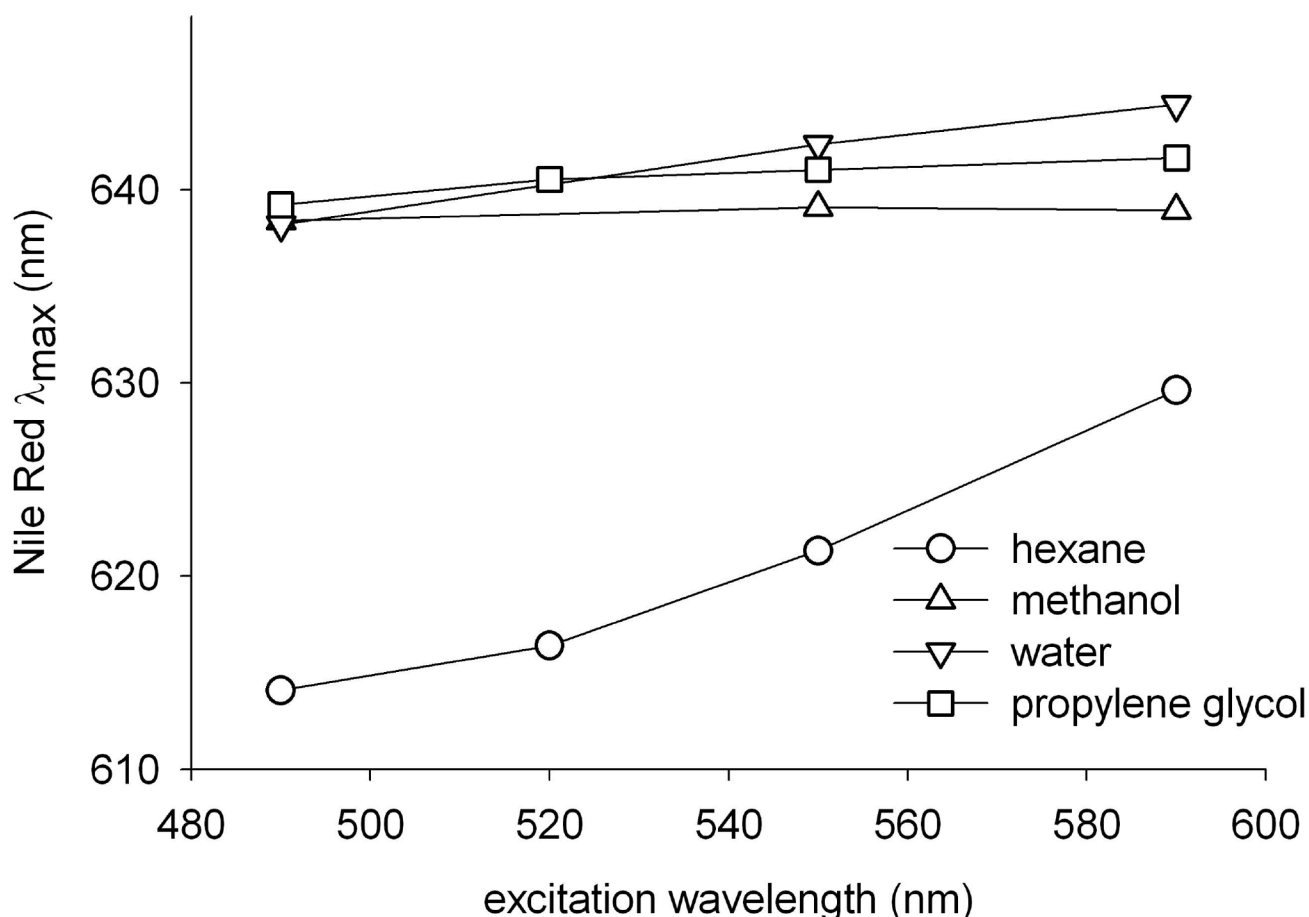


FIG. 3. Excitation-dependent emission of Nile Red in 10% (w/w) surfactant A in water, propylene glycol, methanol and hexane.

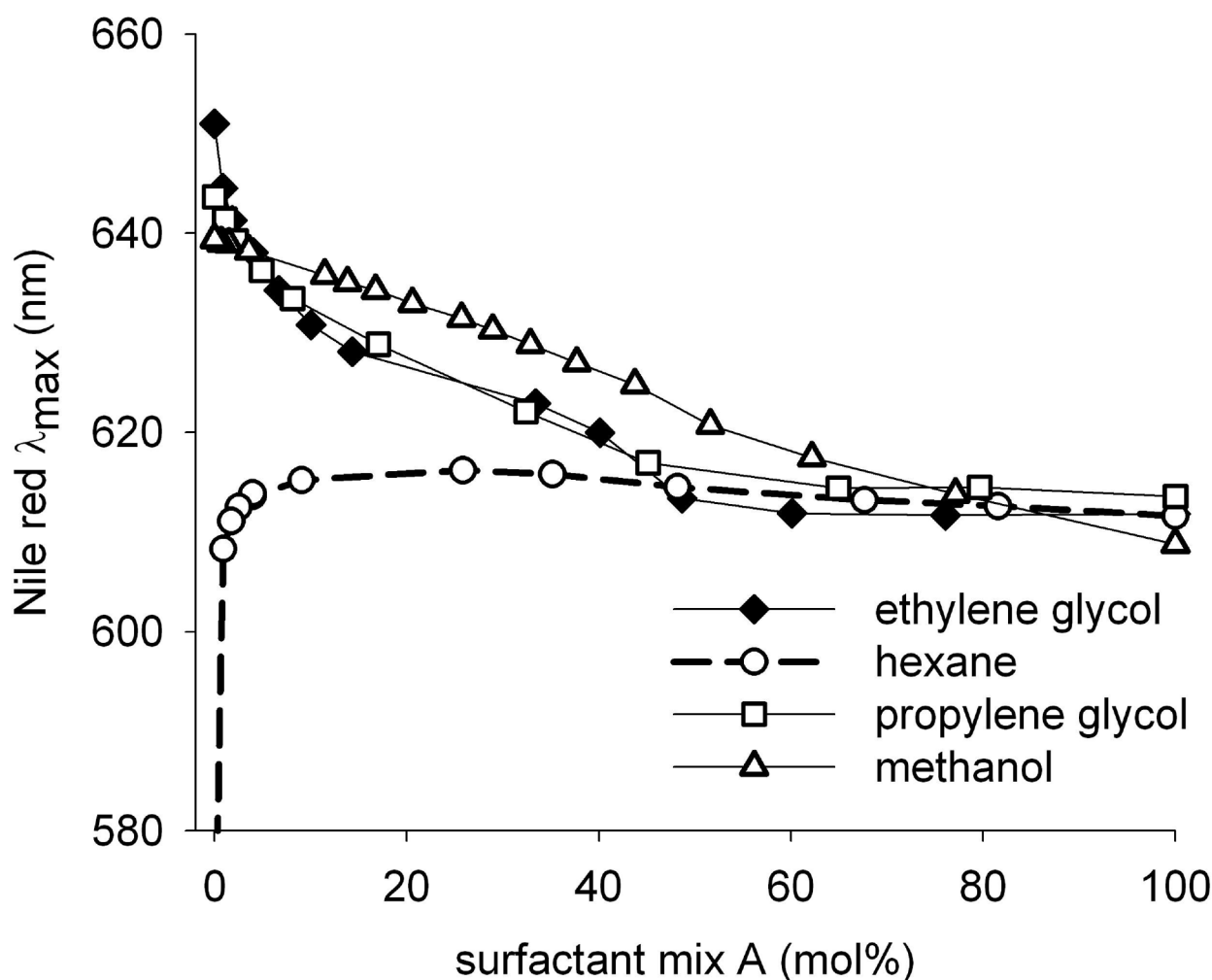


FIG. 4. Change of the λ_{\max} of Nile Red as a function of the surfactant concentration in various solvents.

stayed low until about 50 mol% surfactant (85% w/w), and then an increase in λ_{\max} was observed. The Nile Red emission spectrum has two overlapping peaks in this region, indicating a mixed population of two different aggregated states. Apparently in this region the overall polarity allows the coexistence of inverted micelles and normal micelles. Although coexistence of micelles and inverted micelles is unusual, both structures seem to be stable side by side for at least a couple of days. Upon further dilution with ethylene glycol, λ_{\max} increases to a second plateau. This reflects the region in which normal micelles are present. In methanol, where no surfactant aggregation is expected, λ_{\max} is almost linearly related to the dilution factor. At high surfactant concentrations the presence of inverted micelles gives a slight deviation until they have completely disappeared at around 40 mol% methanol. In propylene glycol there is little evidence for the formation of micelles. The λ_{\max} for propylene glycol is almost, but not completely, linear with the surfactant mix A concentration from the point where inverted micelles are no longer present (around 40 mol% surfactant). The formation of micelles in nonaqueous solvents is driven by solvophobic interactions, which

decrease gradually with the Gordon parameter, so no sharp border is expected between solvents in which surfactant aggregation takes place and solvents in which it does not. In solvents that are more polar or that have a higher cohesive energy density than propylene glycol, the formation of aggregated structures is more clearly observed. These solvents include, from low to high cohesive energy density, monoethanolamine, dimethyl sulfoxide, ethylene glycol, glycerol, and formamide.

DISCUSSION

On the basis of the complex ternary phase behavior of laundry detergent mixtures, the effect of solvents on the size of the LC area and the aggregated state of the surfactant in optically isotropic regions has been investigated.

The size of the LC area was found to be much smaller in all solvents that were examined as compared with water. Moreover, the influence of water is stronger than anticipated in water-solvent mixtures.

The influence of the solvent on the LC phase is clearly correlated with the cohesiveness of the solvent, as was

demonstrated for the Gordon parameter (16,17) and for the Hildebrand parameter (18). Using the solvent polarity scale (π^*) of Kamlet *et al.* (19), the data could be fitted equally well (not shown). Earlier work revealed a clear relation between the cohesive energy density and the surface tension of solvents (17,20,21):

$$(\Delta H_{ev}/V)^{1/2} = k(\gamma/V^{1/3})^{0.43} \quad [1]$$

In this equation, $(\Delta H_{ev}/V)^{1/2}$ is the Hildebrand parameter (heat of evaporation per molecular volume), k is a temperature-dependent constant, and $\gamma/V^{1/3}$ is the Gordon parameter (surface tension per molar volume^{1/3}). If water is mixed with a solvent, the LC area is larger than the average of the two LC areas (of water and the solvent). This indicates the strong preferential interaction of water with the surfactant stabilizing the LC state. If two solvents are mixed (glycerol and *t*-butanol, data not shown), the size of the LC area behaves linearly with the mol fraction of the two solvents (in the ternary phase diagram, a straight line between the points on both solvent axes). The decrease in the LC area has previously been ascribed to dehydration of the head group of nonionics by glycerol and solvent penetration into the aggregates for propylene glycol and propanol (22). A decrease in the Gordon parameter has previously been linked to an increase in the CMC in water-alcohol and in water-hydrazine mixtures (22,23).

Surfactant aggregation providing conventional micelles can be demonstrated, with Nile Red as the probe, for solvents with a high polarity or high cohesive energy density. In propylene glycol, which has a Gordon parameter of 9.1 mN/m², surfactant aggregation is doubtful. More specifically, solvents with a Gordon parameter larger than approximately 9.5 mN/m² did clearly show the formation of micelles. This is much lower than the Gordon value of 12.5 mN/m² claimed by Evans and Miller to be evidence of aggregation (15). The ability of the surfactant to form aggregates decreases when the solubility of the surfactant molecules increases and therefore the solvophobic driving force to form aggregates decreases. This is of course a gradual scale on which no fixed point can be assigned, and that might be dependent on the surfactant polarity.

The size of the aggregates in polar solvents has been stud-

ied previously and was found to be much smaller than that in water (24). A likely explanation is that the size of the aggregates decreases with increased solubility of the surfactant.

By adding a polar solvent to water or in polar solvent alone, the formation of the LC phase can be avoided and a remarkable coexistence region of inverted micelles and normal micelles is observed.

Based on the phase behavior in the ternary mixtures and the results obtained by Nile Red fluorescent spectroscopy, three different situations are envisioned: (i) surfactant aggregation into micelles in a solvent without the formation of an LC phase on the solvent axis (e.g., ethylene glycol); (ii) no surfactant aggregation in pure solvent (e.g., methanol); and (iii) surfactant aggregation in a solvent with the LC area extending over the full width of the ternary phase diagram (e.g., glycerol) (Fig. 5).

Depending on the surfactant/water/solvent system, an LC-free dilution in water can be obtained going either from a nonaggregated state in a solvent to normal micelles in water, or if the surfactant is aggregated into normal micelles in solvent it stays micellar upon dilution into water.

Both the dielectric constant and the Gordon parameter of the solvent can be used to estimate the size of the LC area and the aggregated state of the surfactant.

On diluting practical detergent liquids with water, a large LC area (i.e., poor dissolution behavior) can be avoided by using solvents that are selected based on a relatively low dielectric constant and a relatively low molecular weight.

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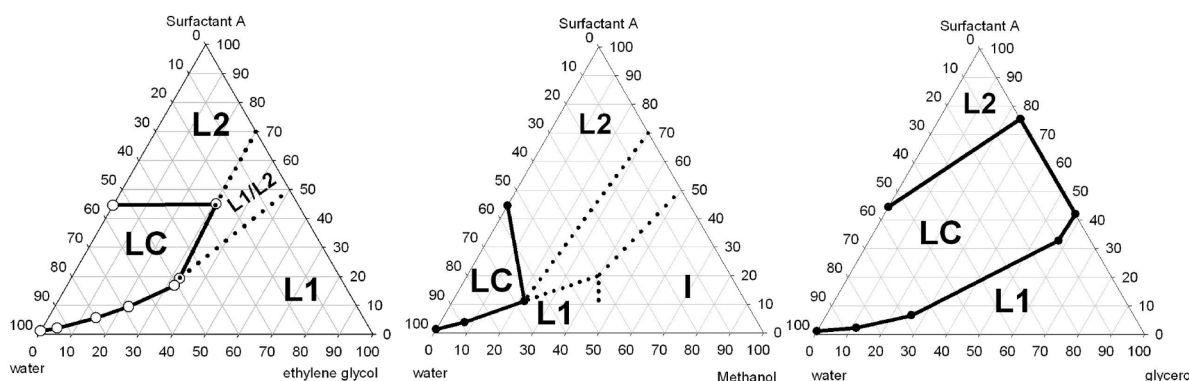


FIG. 5. Ternary phase diagram of surfactant mix A (mole fraction scale) for three solvents: a, ethylene glycol, b, methanol and c, glycerol. L1, normal micelles, L2 inverted micelles, LC, liquid crystalline area and I isotropic (random solution).

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